

ABSORPTION OF WATER AND LUBRICATING OILS INTO POROUS NYLON

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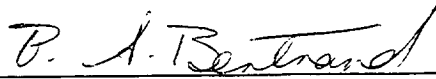
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Abstract

Oil and water absorption from air into sintered porous nylon can be described by infiltration into the pores of the material. This process can be modeled by a diffusion-like mechanism. For water absorption, we find a formal diffusion coefficient of $1.5 \times 10^{-4} \text{ cm}^2/\text{min}$ when the nylon is initially dry. The diffusion coefficient is $4 \times 10^{-6} \text{ cm}^2/\text{min}$ when the nylon is oil-impregnated prior to air exposure. In a 52% RH atmosphere, dry nylon absorbs 3% w/w water, and oil-impregnated nylon absorbs 0.6% w/w water. For oil absorption there are three steps: (1) surface absorption and infiltration into (2) larger and (3) smaller pores. Surface absorption is too fast to be measured in these experiments. The diffusion coefficient for the second step is $6 \times 10^{-4} \text{ cm}^2/\text{min}$ for SRG-60 oil into dry nylon and $4 \times 10^{-4} \text{ cm}^2/\text{min}$ for air-equilibrated nylon. The diffusion coefficient for the third step is about $1 \times 10^{-6} \text{ cm}^2/\text{min}$ for both cases. The total amount of oil absorbed is 31% w/w. The interaction between water and nylon is not as strong as that between water and cotton-phenolic: oil can replace water, and only a small amount of water can enter previously oil-impregnated nylon.

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1. Introduction

Porous nylon, also called "Nylasint," has been used for many years in bearing systems in both space and terrestrial applications. It is often used as a lubricant reservoir, and sometimes as a ball separator (retainer) in ball bearings. This report describes the processes by which both water from the atmosphere and lubricating oil enter the material. The effects of water on oil-filled nylon and of oil on air-equilibrated nylon are also described. The behavior of nylon with respect to water and oil is very different from that of cotton-phenolic, another commonly used retainer material, and similar to the behavior of porous polyimide.

Porous nylon materials are typically made from polyamide powders with particle sizes of 4 to 10 μm . The powders are cold-pressed and then sintered in an inert atmosphere to reduce oxidation of the polymer.¹ Variations in particle size and sintering processes will affect the porosity of the final material. It is well-known that nylon has many pores varying in diameter from 30 to 0.3 μm . The experiments reported herein were carried out on samples from a single nylon tube and with only one oil. In this way, any effects from process variation are minimized; the specific values for rate constants and absorption amounts are, of course, specific to this particular piece of material and this oil.

2. Experimental

The nylon used in these experiments was from a single piece of tube stock that had been made to a specification of 25 to 50% porosity. The material was cleaned by Soxhlet extraction in ethanol overnight, drying in a vacuum oven at 105°C overnight, Soxhlet extraction in heptane overnight, and then again drying in the vacuum oven overnight. Samples were cut with a hand saw from the piece of tube stock. Eight large samples were cut, with heights of about 1.4 to 1.5 cm along the axis of the tube and lengths of about 1.0 to 1.2 cm along the outer curved circumference of the tube and 0.6 to 0.8 cm along the inner curved circumference of the tube. The tube was 0.75 cm thick. These specimens are referred to as samples 1 through 8. Three small samples were cut, one with a height of 1.4 cm and length of about 0.4 cm on each curved edge, and two with heights of about 0.6 cm and lengths of about 0.4 cm on each curved edge. These are referred to as samples 9, 10, and 11. The samples were rinsed in heptane after cutting to remove any loose particles and baked in the vacuum oven overnight immediately before use.

Four sets of experiments were performed.

- Set 1: Samples 1, 2, 3, 4, 9, 10, and 11 were exposed to laboratory air (RH ~ 50%), and weighed periodically.
- Set 2: Samples 5, 6, 7, 8, 9, 10, and 11 were weighed immediately after removal from the oven (9, 10, and 11 had been baked again), then immersed in SRG-60 oil. SRG-60 is a highly refined mineral oil with a viscosity of 77.6 cS at 100°F and a density of 0.8770 g/cm³. The samples were removed periodically, wiped carefully with a lint-free cloth, and weighed.
- Set 3: After samples 1 and 2 had equilibrated with air (i.e., their weight no longer changed with continued exposure), they were immersed in SRG-60 oil, and their absorption of oil was monitored.
- Set 4: After samples 7 and 8 had equilibrated with oil, they were placed in a controlled-humidity environment. The relative humidity of 52% was controlled by a saturated aqueous solution of NaHSO₄•H₂O. They were removed periodically, wiped, and weighed.

3. Results and Discussion

3.1 Infiltration Model

Infiltration into isotropic porous media with interconnected pores can be modeled in a formal sense as a diffusion process. In the process under study here, the absorption of either water from the air or oil continues until the sample is saturated. The appropriate solution of the diffusion equation for saturation of a plane sheet is²

$$\frac{M_t}{M_{\text{sat}}} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp \frac{-D(2m+1)^2 \pi^2 t}{\ell^2}$$

where M_t is the uptake at time t , M_{sat} is the saturation uptake, ℓ is the sample thickness (in these experiments, half the sample thickness since the sample fills from both sides and we ignore the edge effects), D is the formal diffusion coefficient, and m is an index. D is related to the porosity of the matrix and the permeability of the matrix-fluid system, which may be related to the viscosity. The specific dependence of D on the viscosity is influenced by the exact flow process (whether it is viscous and whether there are capillary, electrical, chemical, or other forces involved) and is not predictable in most cases.

3.2 Water Absorption into Dry Nylon

The absorption of water from laboratory air is illustrated in Figure 1. The weight increase can be fit by the infiltration model with a formal diffusion coefficient of $1.5 \times 10^{-4} \text{ cm}^2/\text{min}$. Figure 1a shows the results for the large samples (numbers 1, 2, 3, and 4), with $\ell = 0.38 \text{ cm}$. Figure 1b shows the results for the small samples (numbers 9, 10, and 11), with $\ell = 0.2 \text{ cm}$. The data for the small samples are more scattered than those for the large samples because the amount of water absorbed is very small. However, the infiltration model with the same diffusion coefficient as for the large samples clearly fits the data.

The amount of water in nylon at equilibrium with 50% RH air is 2.8% w/w. This is similar to porous polyimide³ (2.2% w/w) and different from cotton-phenolic⁴ (4.6% w/w).

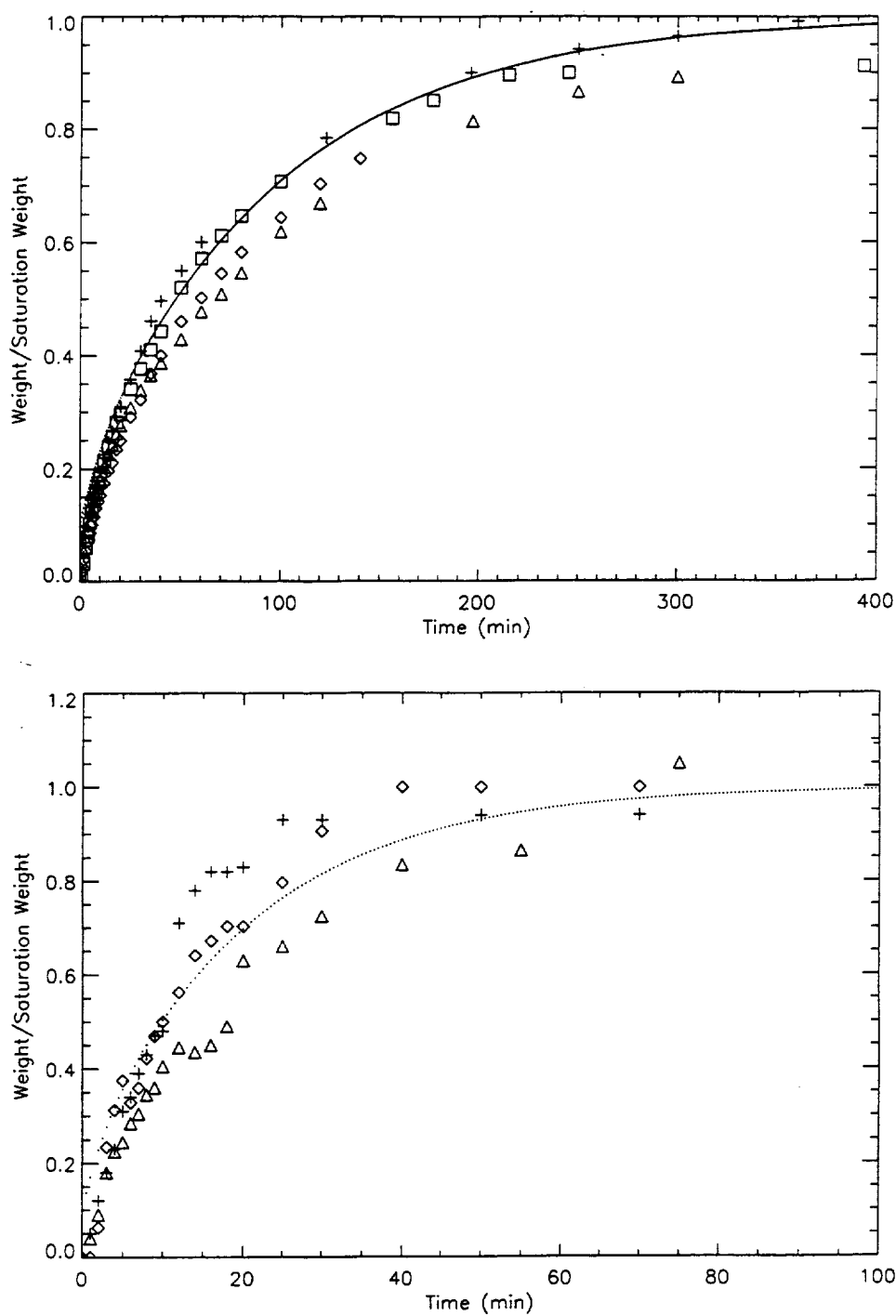


Figure 1. Water absorption into dry nylon. The curves are the best fit of a formal diffusion model to the data. (a) Samples with thickness 0.76 cm. Each symbol represents a different sample. (b) Samples with thickness 0.4 cm. Each symbol represents a different sample. Note different time scales.

3.3 Oil Absorption into Dry Nylon

Over a limited period of time, diffusion-like processes can be fit to a simple absorption amount vs. $t^{1/2}$ relationship. Oil uptake data for Sample 5, which are typical of all the samples, are presented in this way in Figure 2. The absorption appears to be a three-step process. The line representing the second step intersects the ordinate at a non-zero value; this is probably due to a very fast first step, probably adsorption on the external surfaces as well as in very large pores. It amounts to 10 to 40 mg in the large samples and 6 to 13 mg in the small samples, or about 10% of the final saturation amount of oil absorbed. The line representing the third step intersects the ordinate at the weight of oil present at saturation of the second step. This is 185 to 210 mg for the large samples and 37 to 75 mg for the small samples (these numbers include the initial surface absorption and represent about 85% of the saturation amount of oil absorbed). The last few points (corresponding to times greater than 40,000 min) do not lie on the second line. This shows saturation of the sample with oil. Each step will be examined separately below.

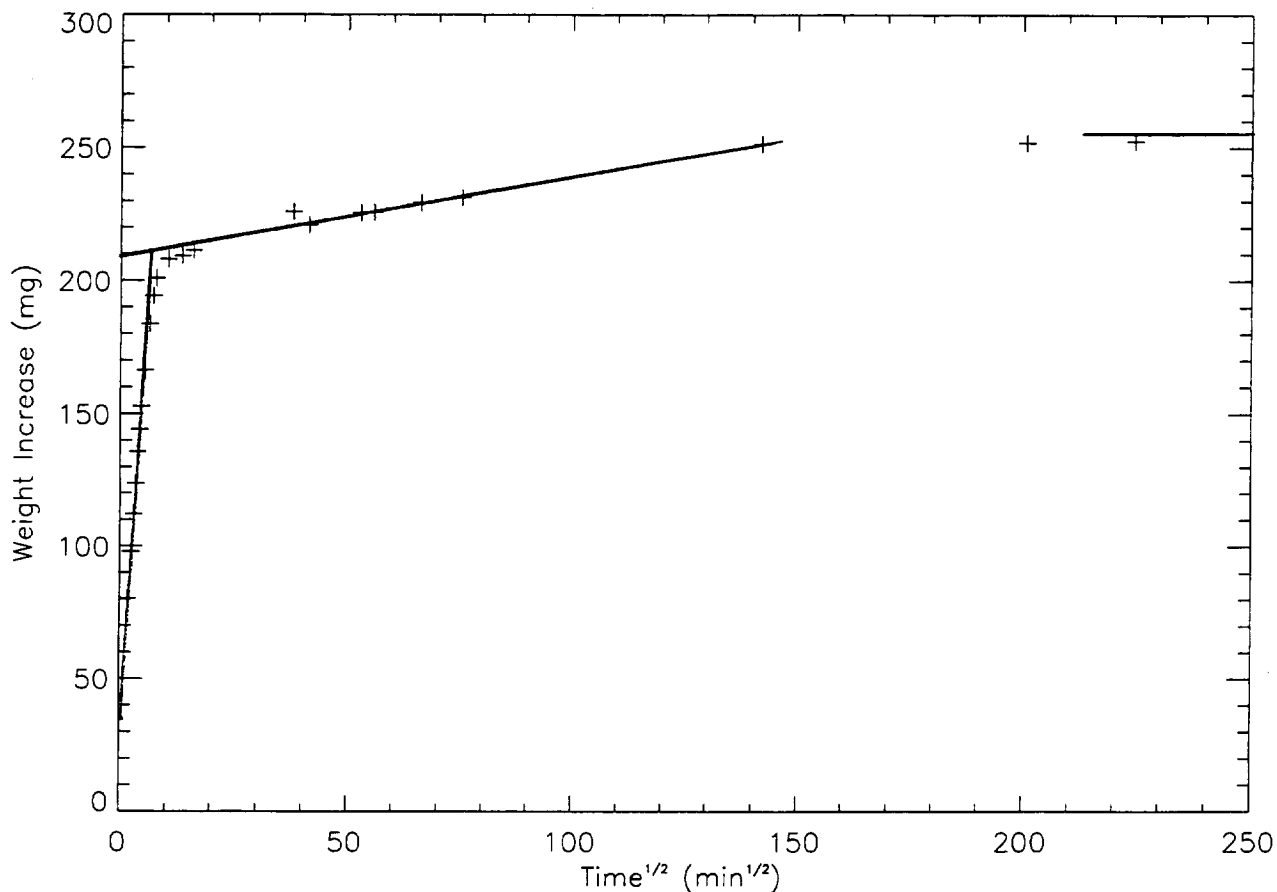


Figure 2. Oil absorption into a typical sample (sample 5) of dry nylon.

Water absorption from air did not show this three-step behavior. This is probably because the water is infiltrating as a gas, while the oil is a liquid. The driving force for the two processes is probably different, with capillary and viscous forces probably contributing more heavily to the oil absorption case.

Figure 3a presents the data for the second step of oil absorption for the large samples: Samples 5, 6, 7 and 8 with $\ell = 0.38$ cm. The weight increase due to the first step, surface and large-pore absorption, has been subtracted from the points. The curve is the best fit of the equation to the data and results from $D = 6 \times 10^{-4}$ cm²/min (1×10^{-5} cm²/s). Previously, we measured $D = 7 \times 10^{-4}$ cm²/min for an oil of viscosity 120 cS at 100°F into porous polyimide.³ The values are very close, showing the similarity of the oil absorption process for the two materials. The oil absorption process in cotton-phenolic cannot be compared directly to the process in porous nylon or polyimide because it follows a different mechanism. The saturation amount of oil absorbed by nylon in this step, including the surface and large-pore term, is $26 \pm 1\%$ w/w.

Figure 3b presents the data for this step for the small samples: Samples 9, 10, and 11 with $\ell = 0.2$ cm. Samples with a different thickness were used to check the dependence of the filling process on the external dimensions of the sample. As one can see by examining the equation, the amount of uptake at a time t (normalized to the saturation amount) is dependent on ℓ , the distance through which the infiltration is taking place. If the filling takes place throughout the pore system, the kinetics will scale with the sample size: ℓ will be half the external sample thickness, and smaller samples will fill faster. However, if the filling is internal to the small nylon particles of which the samples are made (for instance, diffusion of oil into each particle), then ℓ will be half of the small particle size and will be unchanged with the sample's exterior size. In that case, the normalized uptake will not vary with the sample's exterior size. In the experiments, the small samples fill much more quickly than the large ones. The curve was calculated from the equation using the same D we determined for the large samples, 6×10^{-4} cm²/min, and $\ell = 0.2$ cm. The curve fits the data beautifully. This supports the model of oil absorption by infiltration into the pores. The amount of oil absorbing in the first and second steps for the small samples is the same as for the large samples, $26 \pm 1\%$ w/w.

The third step of the oil absorption process is detailed in Figure 4. The oil absorption due to the first and second steps has been subtracted from the total amount of oil absorbed, and the data are plotted from the onset of the third step. The large samples absorb an additional 5% w/w in this step, and the formal diffusion coefficient for the process is 1.5×10^{-6} cm²/min. The data and the model curve are given in Figure 4a. Figure 4b shows the data and model curve for the small samples. They also absorbed an additional 5% w/w in the third step, and the best fit is found using the same diffusion coefficient, 1.5×10^{-6} cm²/min, and a thickness of 0.2 cm. Thus, the third step scales with the overall dimensions of the sample as did the second. The third step is probably absorption into smaller pores, and not diffusion into the nylon particles themselves.

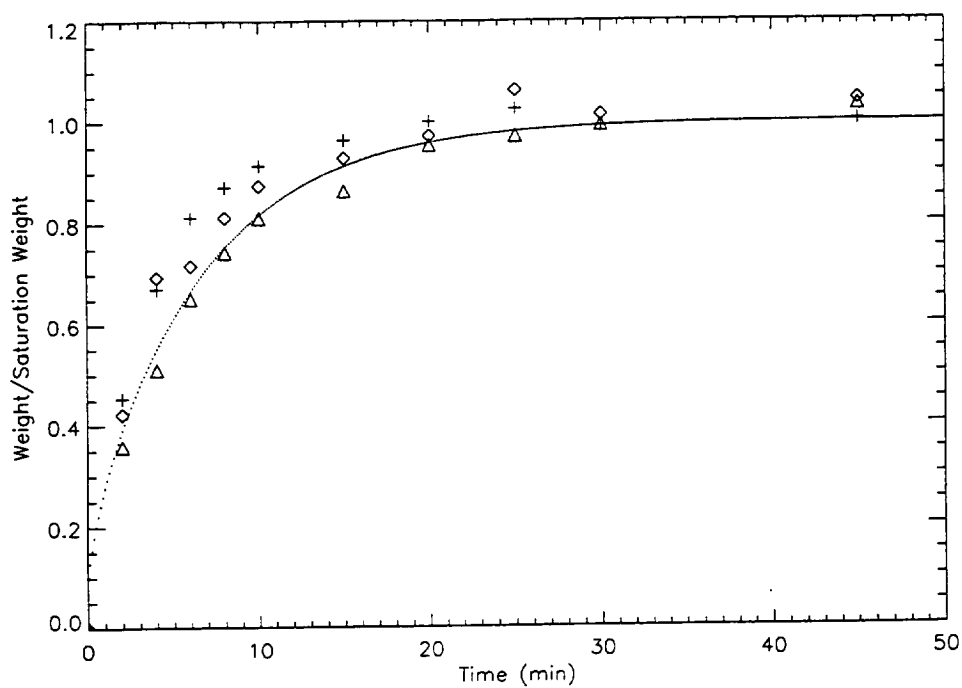
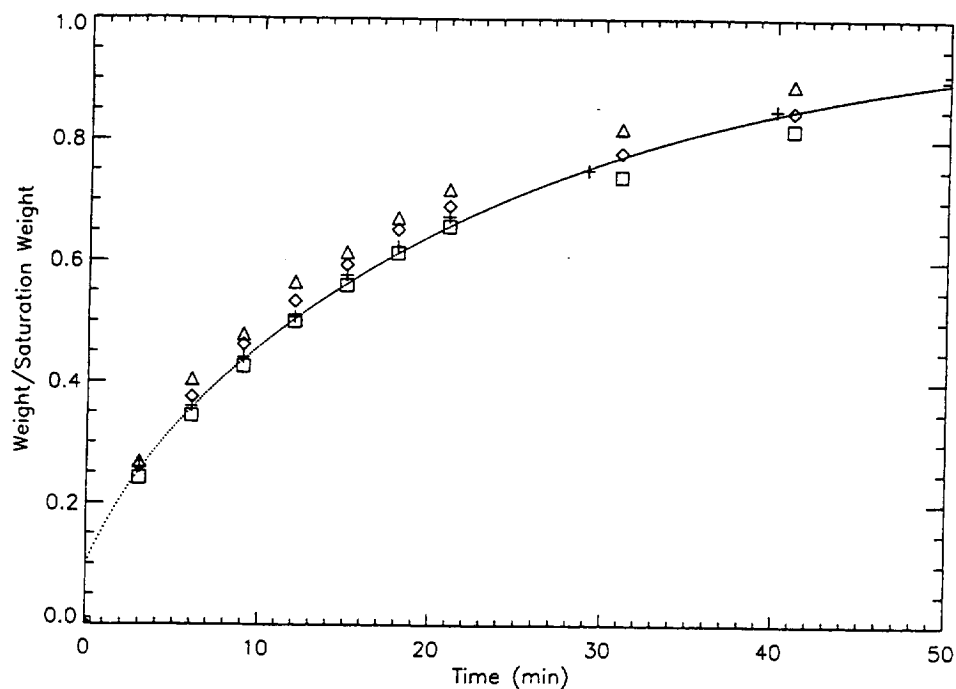


Figure 3. The second step of oil absorption into dry nylon. The curves are the best fit of a formal diffusion model to the data. (a) Samples with thickness 0.76 cm. Each symbol represents a different sample. (b) Samples with thickness 0.4 cm. Each symbol represents a different sample.

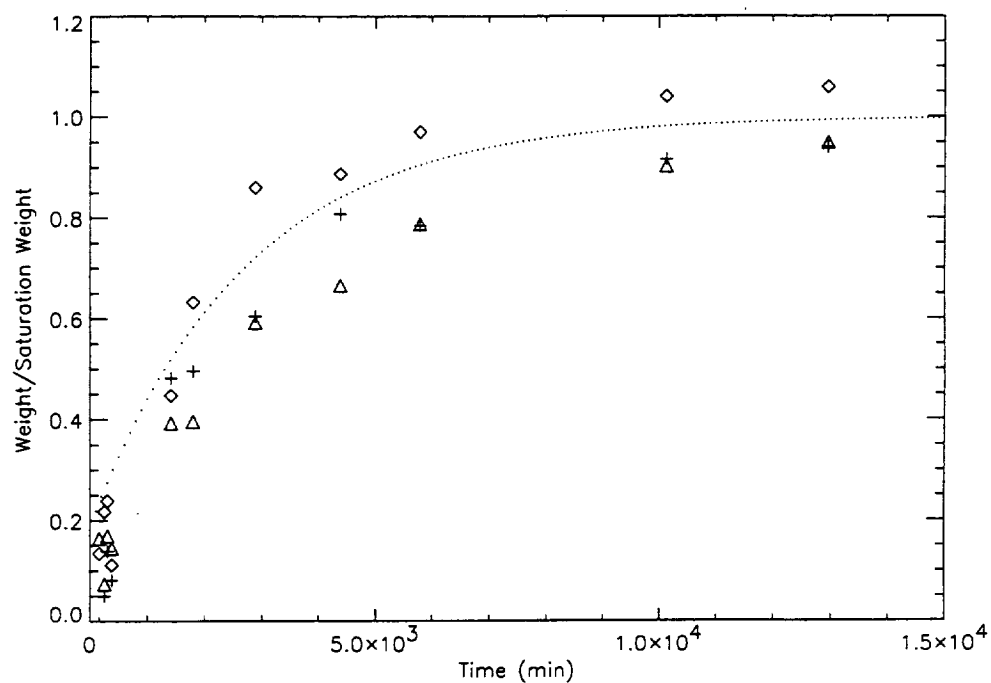
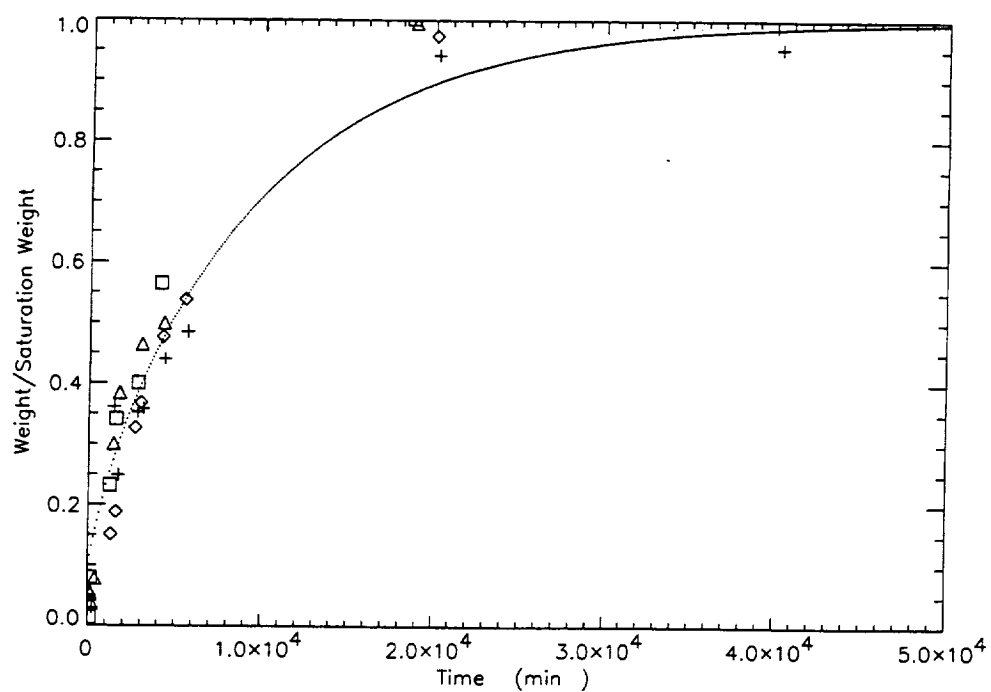


Figure 4. The third step of oil absorption into dry nylon. The curves are the best fit of a formal diffusion model to the data. (a) Samples with thickness 0.76 cm. Each symbol represents a different sample. (b) Samples with thickness 0.4 cm. Each symbol represents a different sample.

3.4 Oil Absorption into Air-equilibrated Nylon

Samples 1 and 2 were placed in a bath of SRG-60 oil after they had equilibrated with laboratory air (RH ~50%). The presence of water in the nylon slowed the absorption of oil, but did not significantly affect the overall amount of oil absorbed. Oil absorption remained a three-step process.

Figure 5 shows the data and model fit for the second step of oil absorption into air-equilibrated and dry nylon. The formal diffusion coefficient for the air-equilibrated case is 4×10^{-4} cm²/min, which is $\frac{2}{3}$ of that for the dry case. The weight gain (relative to dry nylon) in the air-equilibrated case is $26 \pm 1\%$ w/w, just as in the dry case. Either the water remained in the sample, and a lesser weight of oil was absorbed in the air-equilibrated case (i.e., 3% w/w water remained, and 23% w/w oil was absorbed), or the water was removed as the oil entered. The oil was probably dry since it had been stored in a desiccator for several weeks, and the absorption experiments were carried out in the desiccator, so it is highly likely that the water was removed in the course of the experiments.

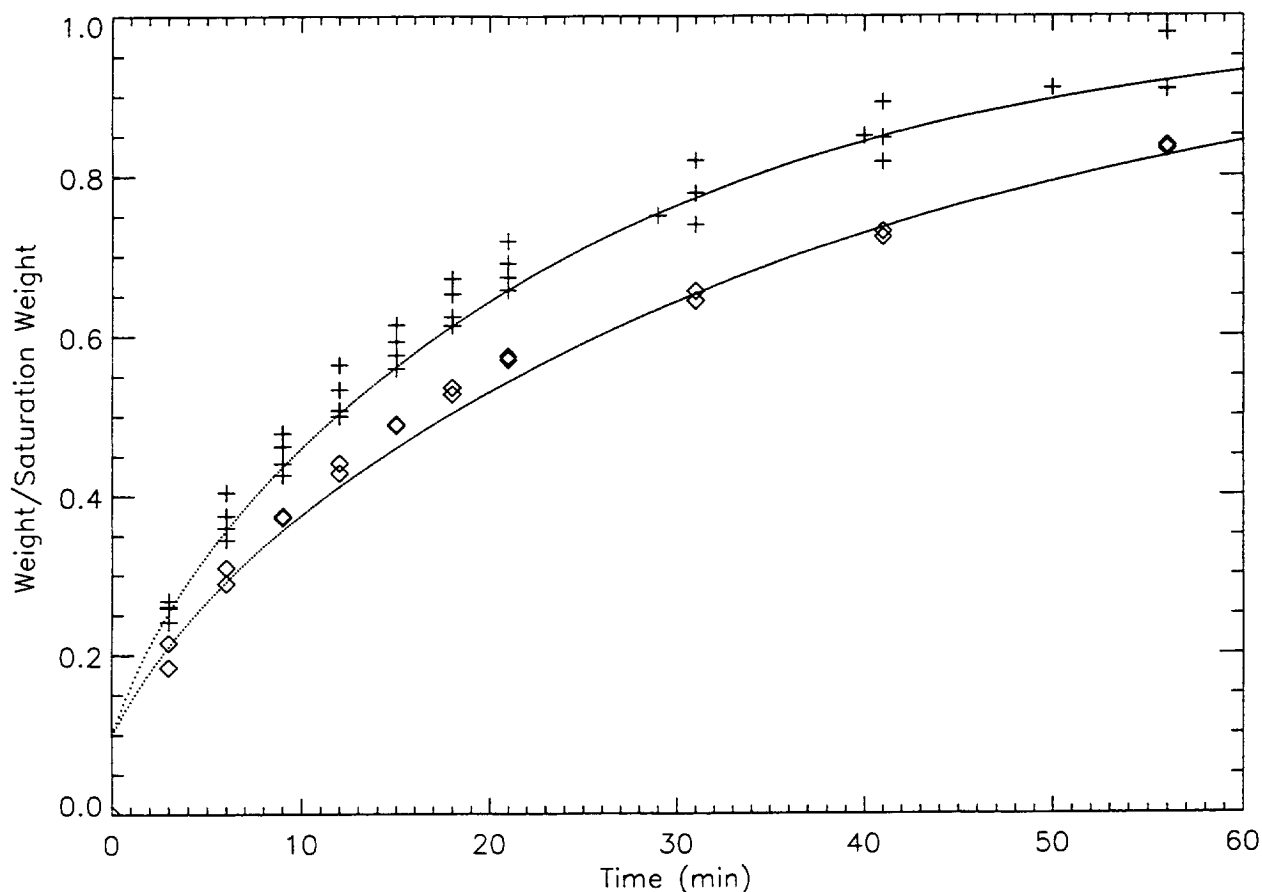


Figure 5. Oil absorption into nylon. + represents samples that were dry before oil absorption, ◇ represents samples that were equilibrated with room air at 50% RH before oil absorption. The curves are the best fit of a formal diffusion model to the data.

Another piece of evidence that the water was removed from the nylon during our experiments is that the third step of the oil absorption process, filling of the smaller pores, has exactly the same kinetics in the air-equilibrated and dry cases. If water were still present, one might expect the diffusion coefficient for oil absorption to be reduced in the third step as it was in the second. This did not occur. The diffusion coefficient was $1.5 \times 10^{-6} \text{ cm}^2/\text{min}$, and the saturation amount was an additional 5% w/w.

3.5 Water Absorption into Oil-impregnated Nylon

Samples 1 and 2 were placed in a controlled humidity environment (52% RH) after they were completely filled with oil. Figure 6 shows the data and the model fit. Water absorption is an infiltration process for both dry and oil-filled nylon. The diffusion coefficient for the oil-filled case is $4 \times 10^{-6} \text{ cm}^2/\text{min}$, or 0.03 times the diffusion coefficient for the dry case: the process is much slower in the oil-filled material. The saturation amount of water absorbed is also much less: 0.6 % w/w in oil-filled nylon compared to almost 3% in dry nylon.

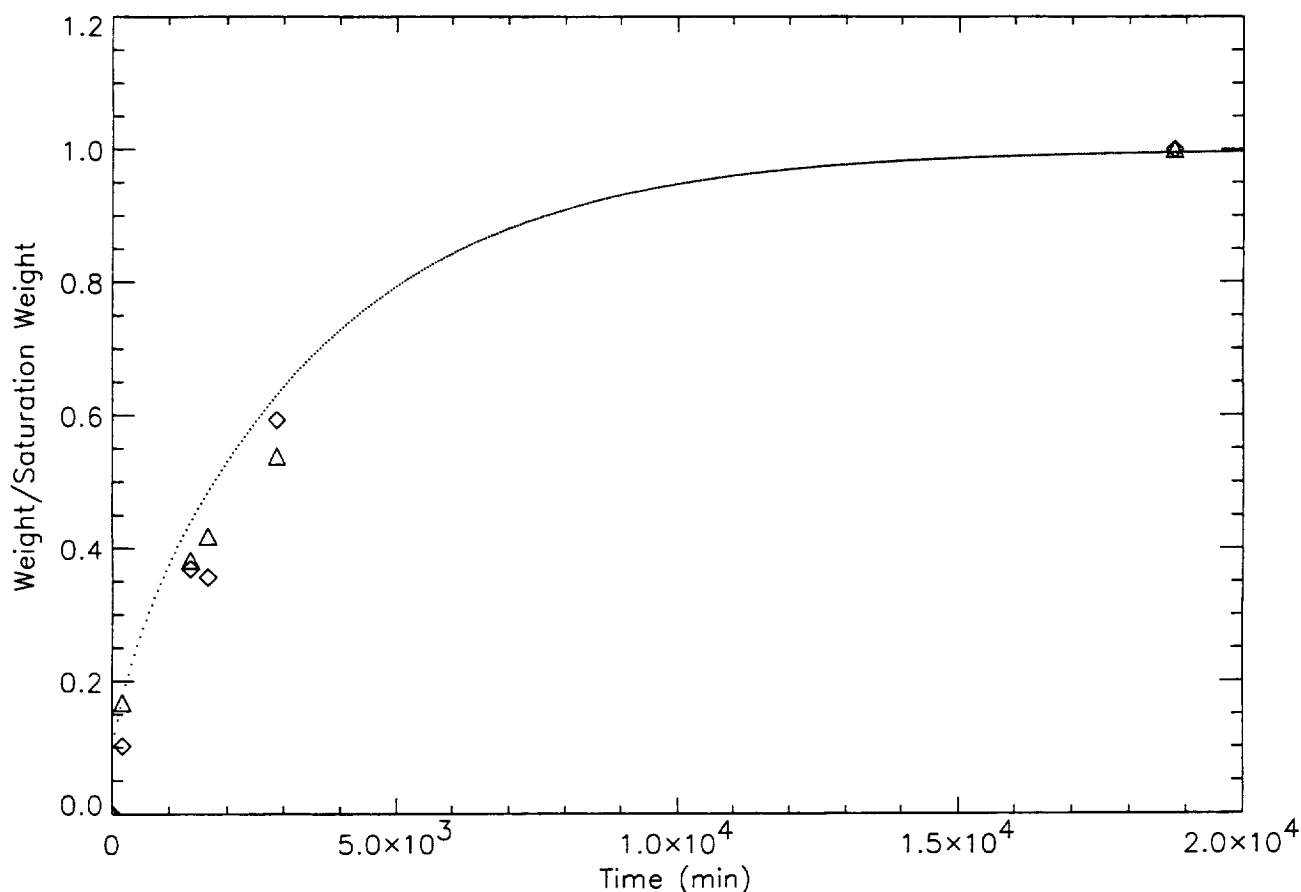


Figure 6. Water absorption into oil-impregnated nylon. Each symbol represents a different sample. The curve is the best fit of a formal diffusion model to the data.

The fact that much less water is absorbed into oil-impregnated nylon is additional evidence that oil probably replaced most of the water in the air-equilibrated nylon that was subsequently placed in oil. This suggests that there is no strong interaction between nylon and water, unlike the very strong interaction between cotton-phenolic and water, which can prevent oil from entering the material at all and remove oil that has been previously absorbed.

When the samples were subsequently placed in a desiccator with CaSO_4 drying agent for a week, their weights returned to the values after filling with oil and before exposure to humid air. Thus, no measurable oil was removed by the water as it absorbed.

4. Conclusions

The absorption of water and oil into nylon is very different from that into cotton-phenolic and similar to that into porous polyimide. Oil and water absorption from air into porous nylon can be described by infiltration into the pores of the material. This process can be modeled by a diffusion-like mechanism. For water absorption, we find a formal diffusion coefficient of $1.5 \times 10^{-4} \text{ cm}^2/\text{min}$ when the nylon is initially dry. The diffusion coefficient is $4 \times 10^{-6} \text{ cm}^2/\text{min}$ when the nylon is oil-impregnated prior to exposure to moist air. In a 50% RH atmosphere, dry nylon absorbs 3% w/w water, and oil-impregnated nylon absorbs 0.6% w/w water. For oil absorption, there are three steps, which probably involve infiltration into pores of varying sizes. The first step, surface absorption and filling of very large pores, is too fast to be measured in these experiments. The diffusion coefficient for the second step, filling of large pores, is $6 \times 10^{-4} \text{ cm}^2/\text{min}$ for dry nylon and $4 \times 10^{-4} \text{ cm}^2/\text{min}$ for air-equilibrated nylon. The diffusion coefficient for the third step, filling of small pores, is about $1 \times 10^{-6} \text{ cm}^2/\text{min}$ for both cases. The total amount of oil absorbed is 31% w/w.

The interaction between water and nylon is not as strong as that between water and cotton-phenolic. Water can prevent the absorption of oil into cotton-phenolic and can drive out oil that has already been impregnated into the material. In nylon, oil can replace water, and only a small amount of water can enter previously impregnated nylon. Thus, the extremely rigorous precautions that must be taken to prevent water absorption by cotton-phenolic need not be taken with nylon unless the small amount of water retained even by impregnated material would cause problems for the final application.

References

1. S. S. Schwartz and S. H. Goodman, *Plastics Materials and Processes*, (Van Nostrand Reinhold Company, New York, 1982).
2. J. Crank, *The Mathematics of Diffusion*, (The Clarendon Press, Oxford, 1957).
3. P. A. Bertrand, "Absorption of Water and Lubricating Oils into Porous Polyimide," TOR-0091(6404-10)-5, The Aerospace Corporation, 15 Nov 1991.
4. P. A. Bertrand, "Absorption of Water by Cotton-Phenolic Retainer Material," TOR-0091(6404-10)-3, The Aerospace Corporation, 30 Sept, 1991.

